Nanoscale Interfacial Engineering for Stable Lithium Metal Anodes

Yi Cui

Stanford University

June 8, 2017

Project ID #ES274

Overview

Timeline

- Start: August 1, 2013
- End: July 31, 2017
- Percent complete: 80%

Budget

- Total project funding
  $1,350k
- Funding received in FY 2016
  $450k
- Funding for FY 2017
  $450k

Barriers

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high-energy electrode materials and batteries

Partners

- Collaboration

- BMR program PI's
- SLAC: In-situ X-ray
- Amprius Inc.
- Professor Steven Chu, Zhenan Bao

Project Objective and Relevance

Objective

- Develop lithium metal anodes with high capacity and reliability for the next-generation high-energy-density rechargeable lithium-based batteries to power electric vehicles (HEV/PEV/EV).

-Design and fabricate novel chemically and mechanically stable interfacial layers between lithium metal and electrolytes to overcome the intrinsic material challenges that lead to short battery life, including lithium metal dendrite formation and severe side chemical reactions during electrochemical cycling.

-Understand the effects of interfacial protection materials and additives on the performance and life time of lithium metal batteries.

- Develop scalable low-cost methods for the synthesis of nanostructured lithium metal anodes and interfacial protection materials.

-Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.

Milestones for FY16 and 17

Month/ year	Milestones	Status
3/2015	Fabrication of interfacial protection materials, including interconnected carbon hollow spheres, layered h-BN and graphene with different thicknesses and defect levels.	Complete
6/2015	Determine the effect of $LiNO_3$ and lithium polysulfide on the cycling Coulombic efficiency of lithium metal anode.	Complete
9/2015	Demonstrate the guiding effect of polymer nanofibers for improved lithium metal cycling performance.	Complete
12/2015	Demonstrate the improved cycling performance of surface-engineered lithium metal anode under different current density and areal capacity.	Complete
3/2016	Achieve minimum relative volume change and effective dendrite suppression during electrochemical cycling via nanoporous host-lithium composite electrode design.	Complete
9/2016	Study the effects of substrate lithium affinity on the nucleation/growth behavior and Coulombic efficiency of lithium metal.	Complete
12/2016	Demonstrate low-cost, scalable fabrication of porous host-lithium composite electrodes.	Complete
3/2017	Demonstrate successful sealing of pinholes in h-BN thin film pinholes.	Complete

Approach/Strategy

Advanced design and synthesis of interfacial protecting layers and nanostructured lithium metal electrodes

1)Engineer various interfacial protection materials with excellent chemical and mechanical stability (interconnected carbon hollow spheres, layered h-BN, graphene, etc.) to suppress lithium dendrite formation during electrochemical cycling and to improve Coulombic efficiency.

2)Develop/discover stable, light-weight host materials with high lithium affinity for the fabrication of nanoporous lithium-host composite electrodes with minimum relative volume change during cycling and improved electrochemical performance.

3)Develop effective surface coating/modification techniques to achieve high lithium affinity on host materials.

4)Control the lithium deposition behavior through nanoparticle seeded growth and nanomaterials encapsulation

Structure and property characterization

1)Ex-situ transmission electron microscopy & scanning electron microscopy

2)In-situ transmission electron microscopy

3)In-situ optical microscopy

4)X-ray diffraction

5)X-ray photoelectron spectroscopy

6)Fourier transform infrared spectroscopy

Electrochemical testing

1) Coin cells and pouch cells

2) A set of electrochemical techniques

Possible Practical Specific Energy Based on Li-Chemistry

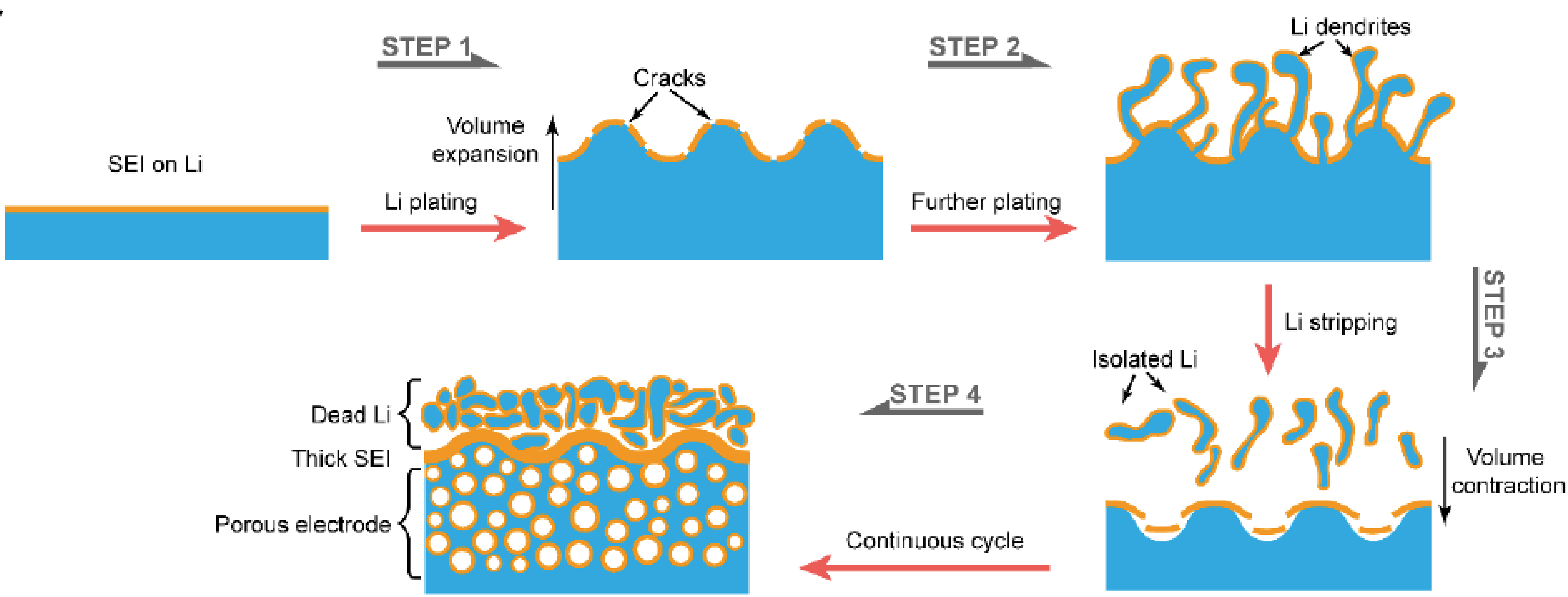
Li meal/sulfur
>600 Wh/kg

Li metal/NMC
500Wh/kg

Si/NMC
400 Wh/kg

Graphite/NMC
300 Wh/kg

Challenges of Lithium Metal Anodes

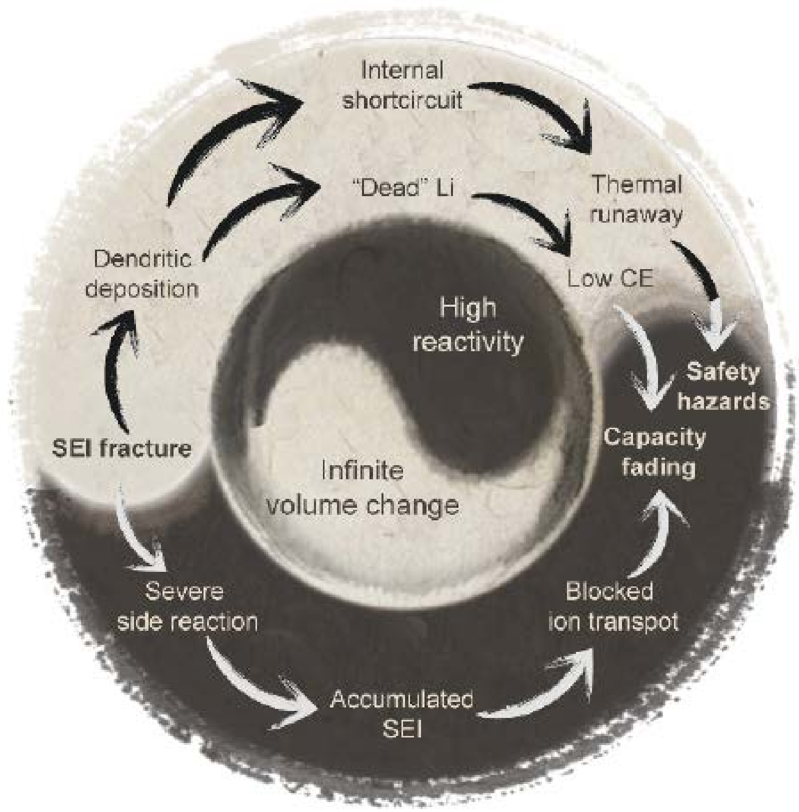


1 mAh/cm^2: 5um
3 mAh/cm^2: 15um

D. Lin, Y. Liu, Y. Cui *Nature Nanotechnology* 12, 194 (2017).

Challenges of Lithium Metal Anodes

Fundamental Root Cause of Li Metal Problems:
1) No Host
2) High chemical reactivity



D. Lin, Y. Liu, Y. Cui *Nature Nanotechnology* 12, 194 (2017).

REVIEW ARTICLE
PUBLISHED ONLINE: 7 MARCH 2017 | DOI: 10.1038/NNANO.2017.16
nature nanotechnology

Reviving the lithium metal anode for high-energy batteries

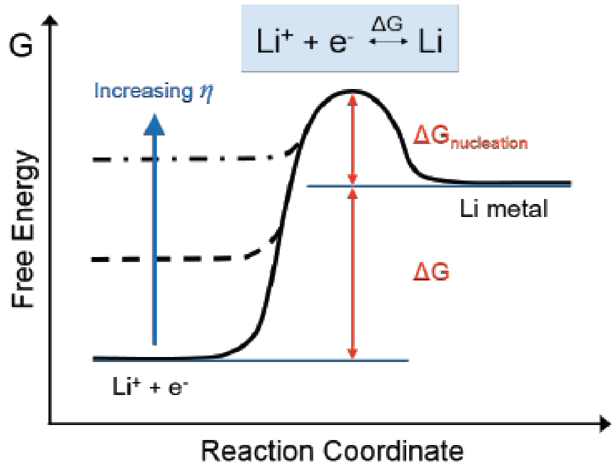
Dingchang Lin[1†], Yayuan Liu[1†] and Yi Cui[1,2*]

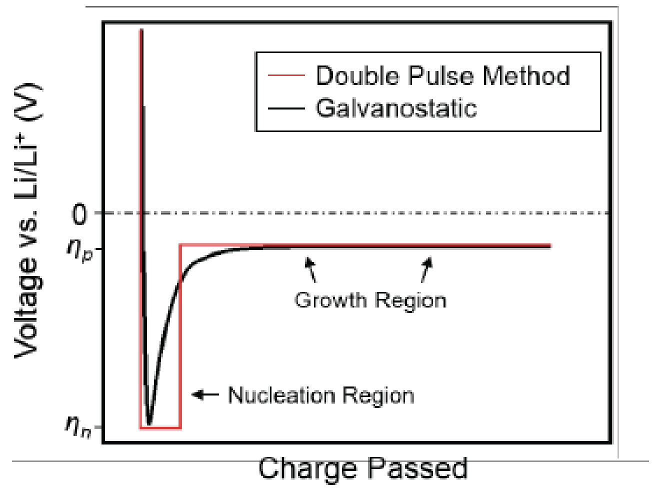
Lithium-ion batteries have had a profound impact on our daily life, but inherent limitations make it difficult for Li-ion chemistries to meet the growing demands for portable electronics, electric vehicles and grid-scale energy storage. Therefore, chemistries beyond Li-ion are currently being investigated and need to be made viable for commercial applications. The use of metallic Li is one of the most favoured choices for next-generation Li batteries, especially Li–S and Li–air systems. After falling into oblivion for several decades because of safety concerns, metallic Li is now ready for a revival, thanks to the development of investigative tools and nanotechnology-based solutions. In this Review, we first summarize the current understanding on Li anodes, then highlight the recent key progress in materials design and advanced characterization techniques, and finally discuss the opportunities and possible directions for future development of Li anodes in applications.

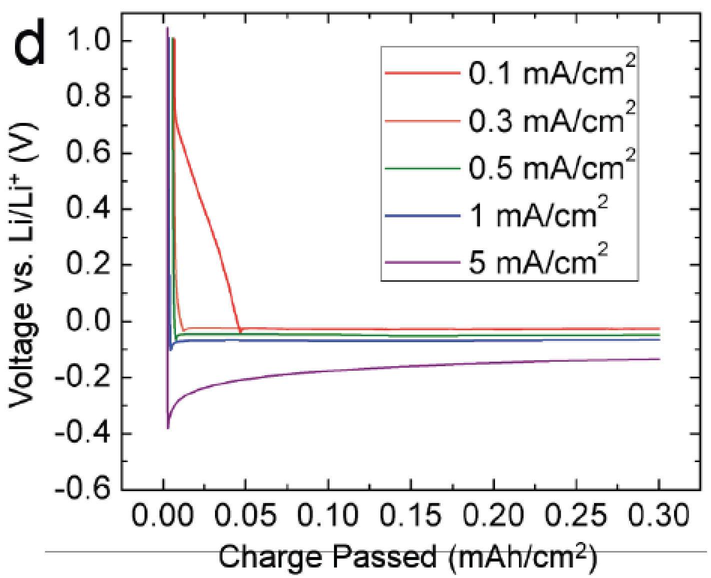
D. Lin, Y. Liu, Y. Cui *Nature Nanotechnology* 12, 194 (2017).

Accomplishments: Li metal nucleation

Li metal heterogeneous nucleation

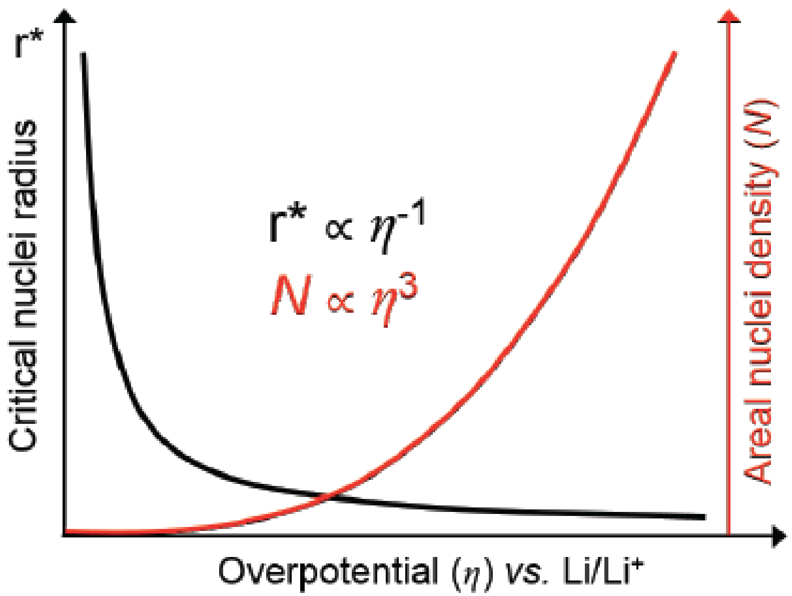


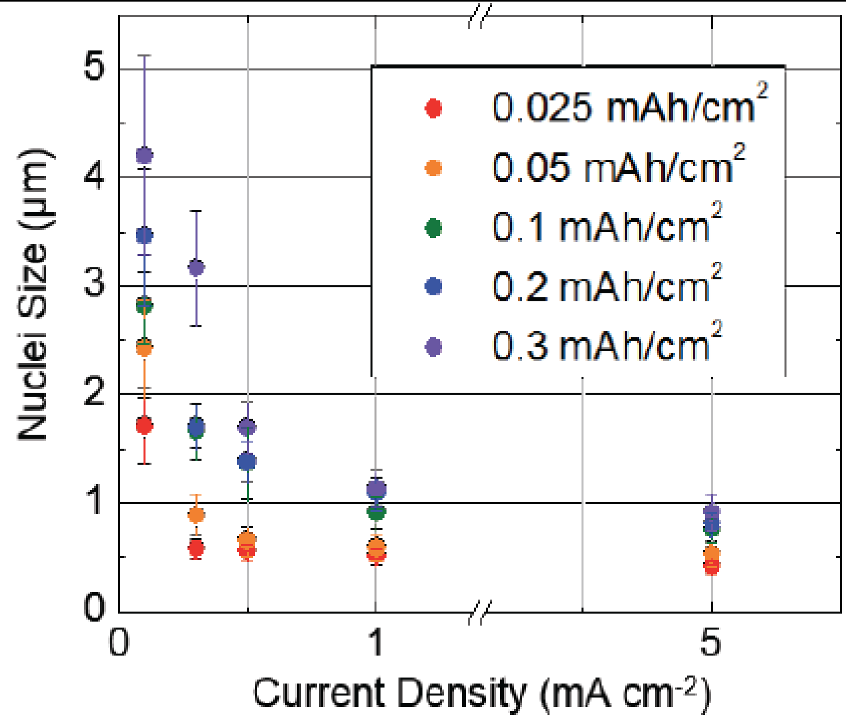


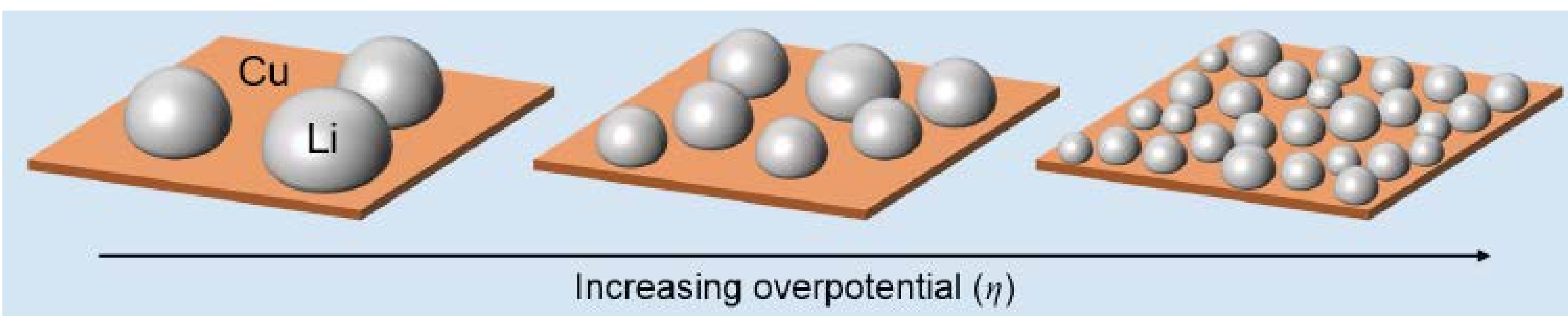


A Pei, Y. Cui *Nano Letters* 17, 1132 (2017)

Accomplishments: Li metal nucleation

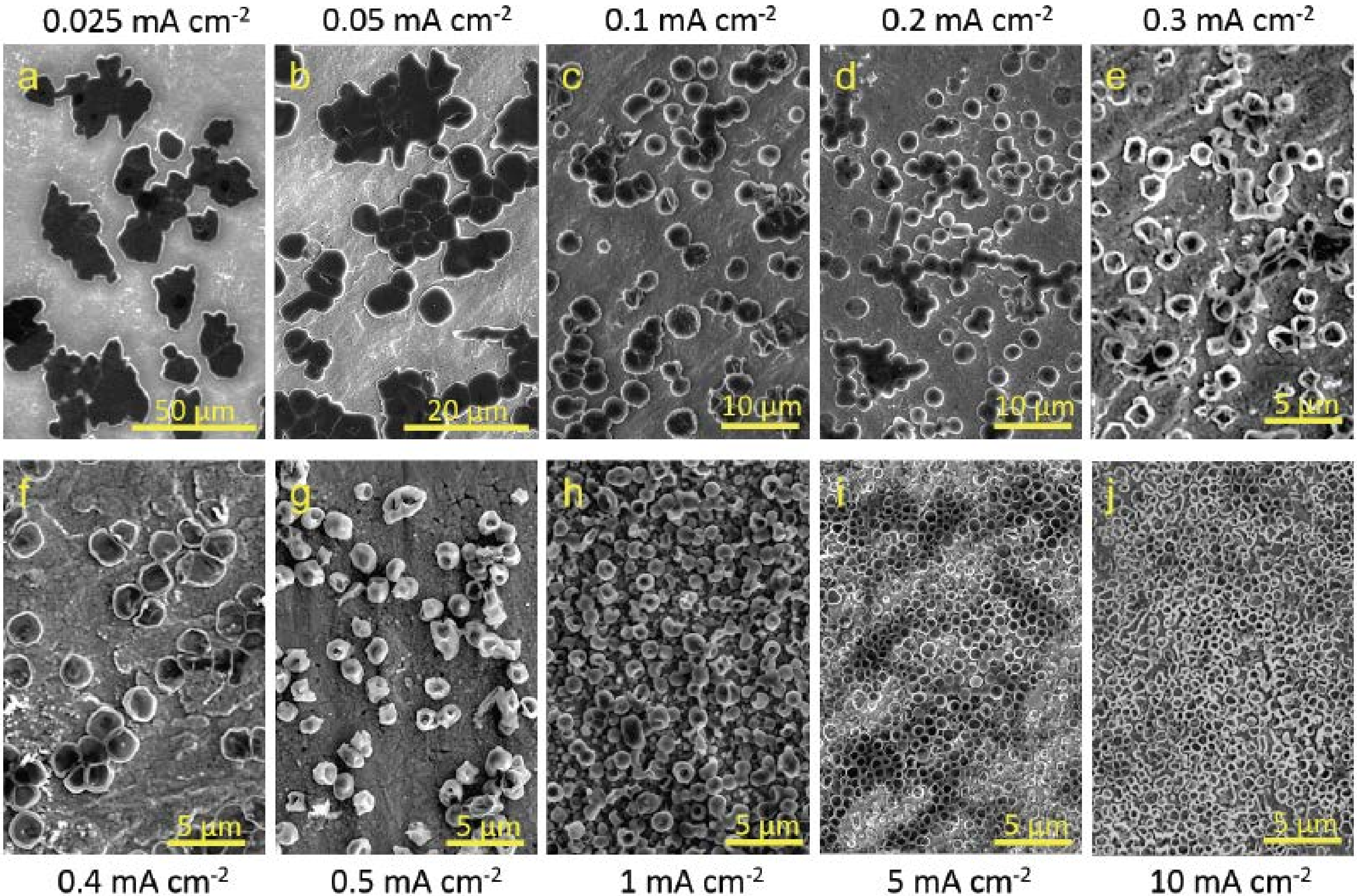






A Pei, Y. Cui *Nano Letters* 17, 1132 (2017)

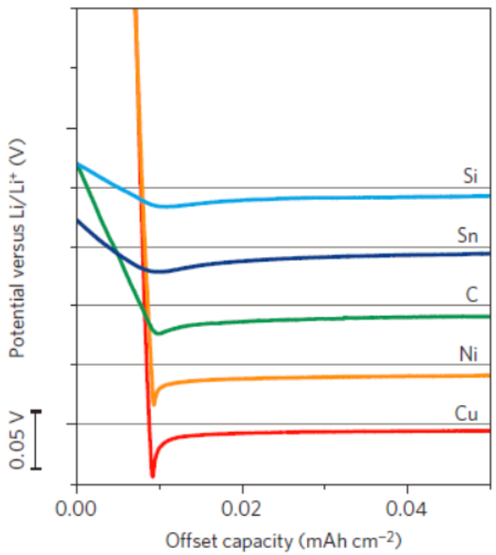
Accomplishments: Li metal nucleation

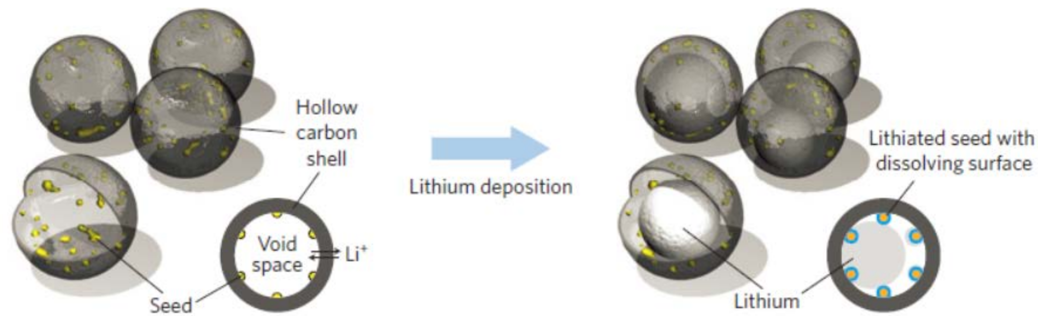


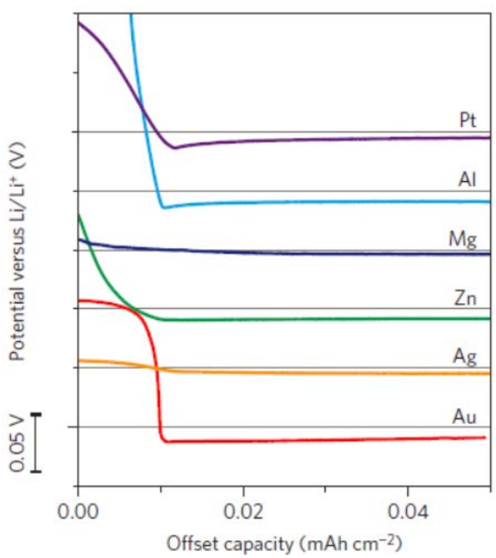
A Pei, Y. Cui *Nano Letters* 17, 1132 (2017)

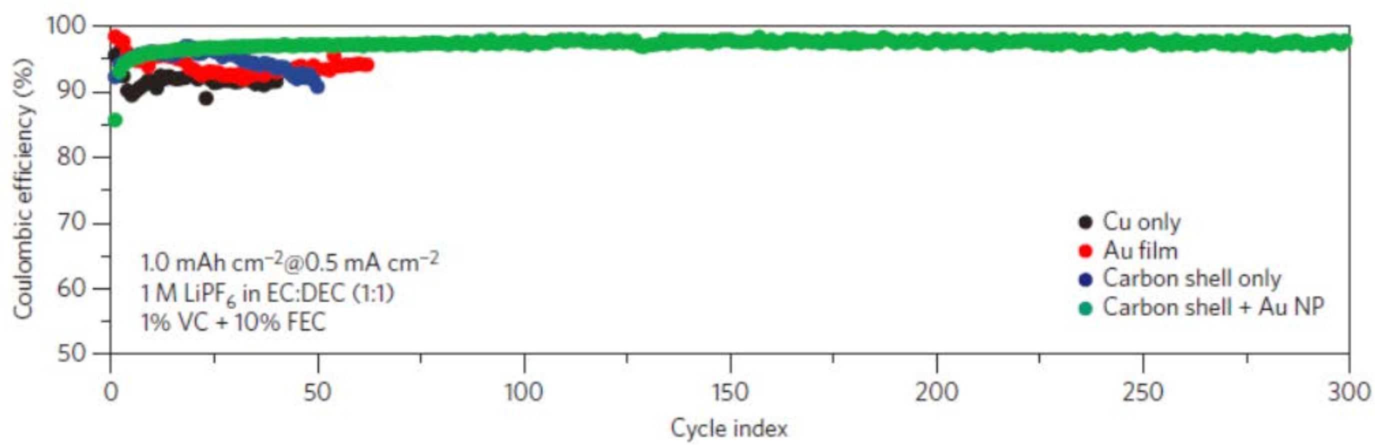
Accomplishments: substrate dependent nucleation

Selective lithium deposition with nano-sized seeds





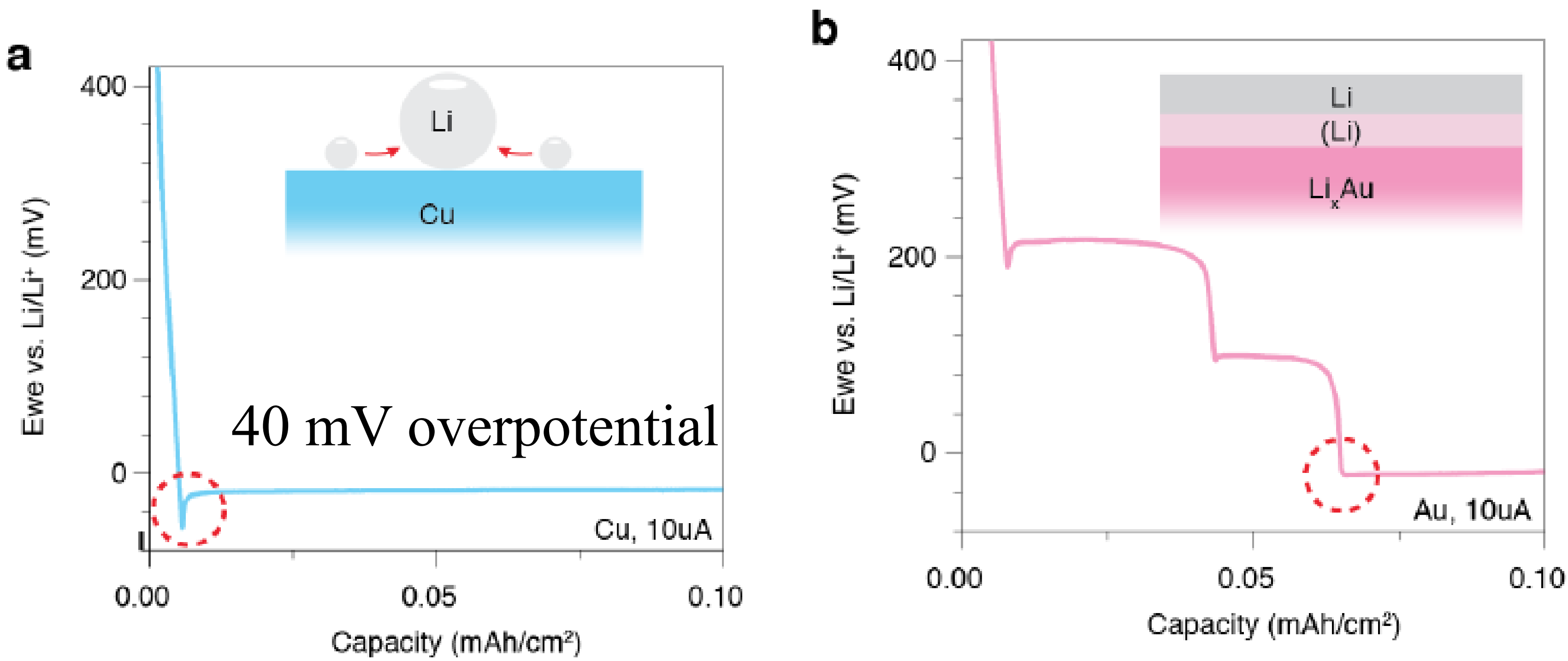




Cui group, *Nature Energy*, **1**, 16010 (2016) (Collaborated with Prof. Steven Chu)

Accomplishments: substrate dependent nucleation

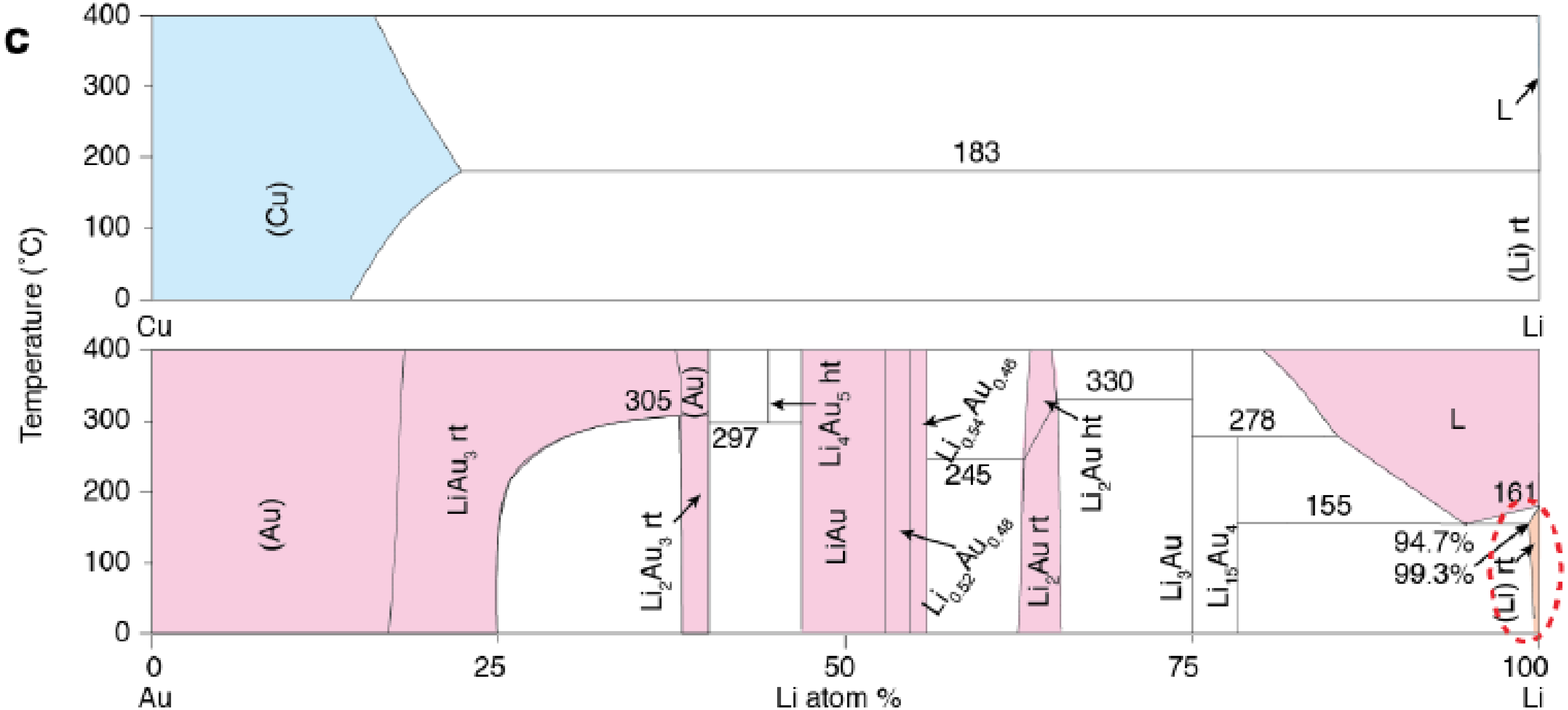
Li metal nucleation on Cu and Au



1 M $LiPF_6$ in EC:DEC

K Yan, S. Chu, Y. Cui *Nature Energy* 1, 16010 (2016)

Phase Diagrams of Li-Cu and Li-Au

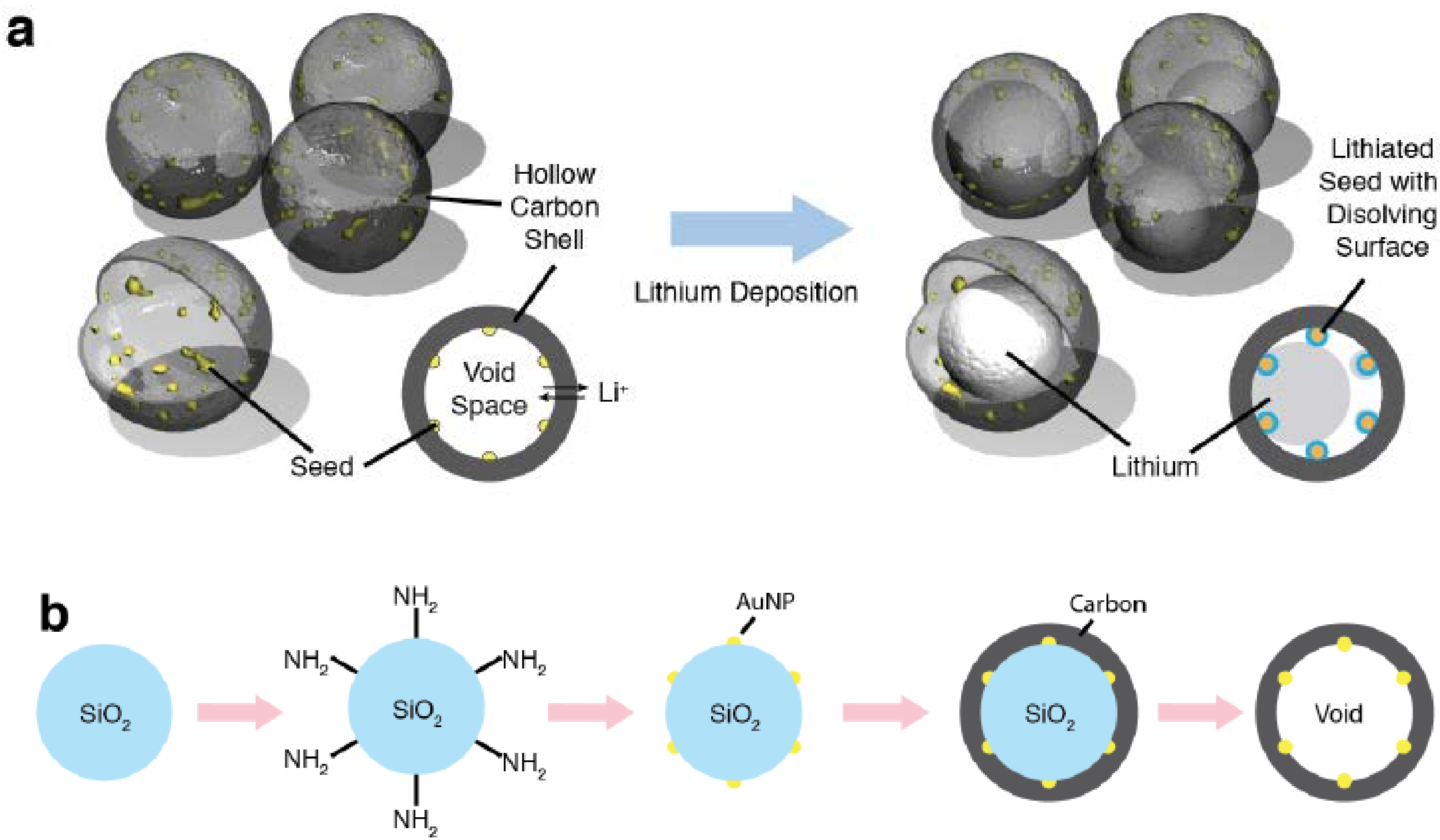


Cu has negligible solubility in Li.
Au has some solubility in Li.

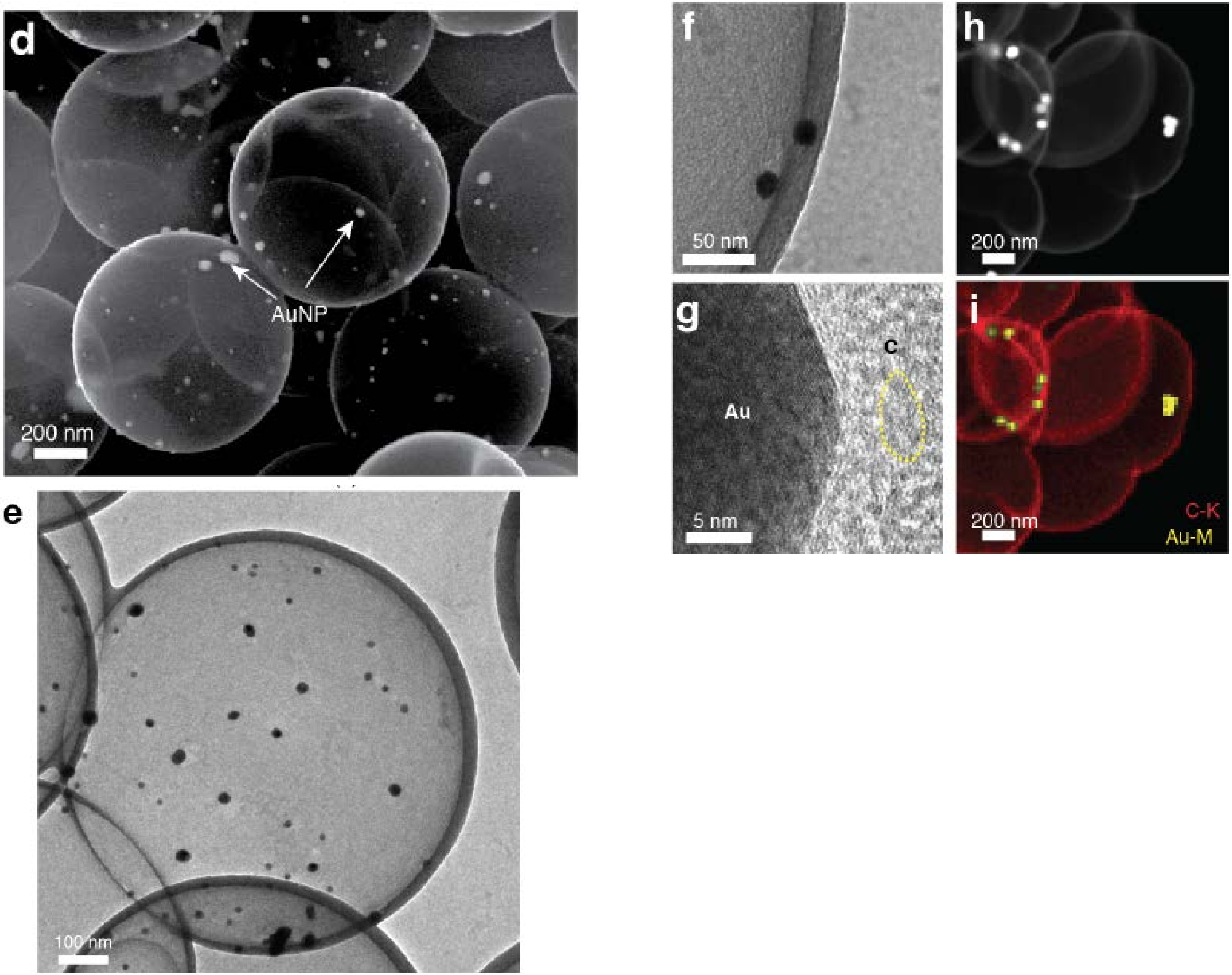
K Yan, S. Chu, Y. Cui *Nature Energy* 1, 16010 (2016)

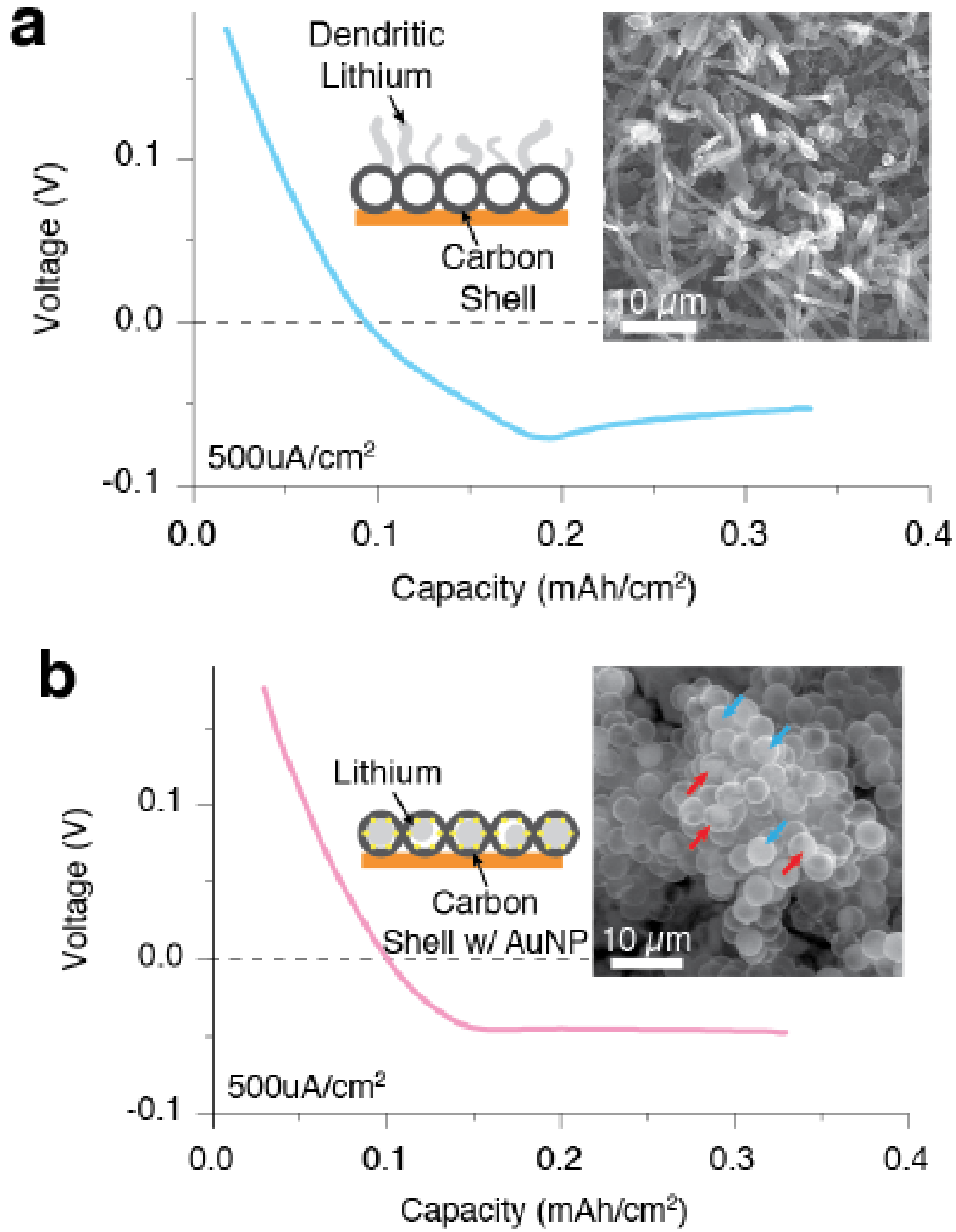
Accomplishments: Seeded Hollow Carbon Host

Nanocapsule as a "Host" for Lithium Metal



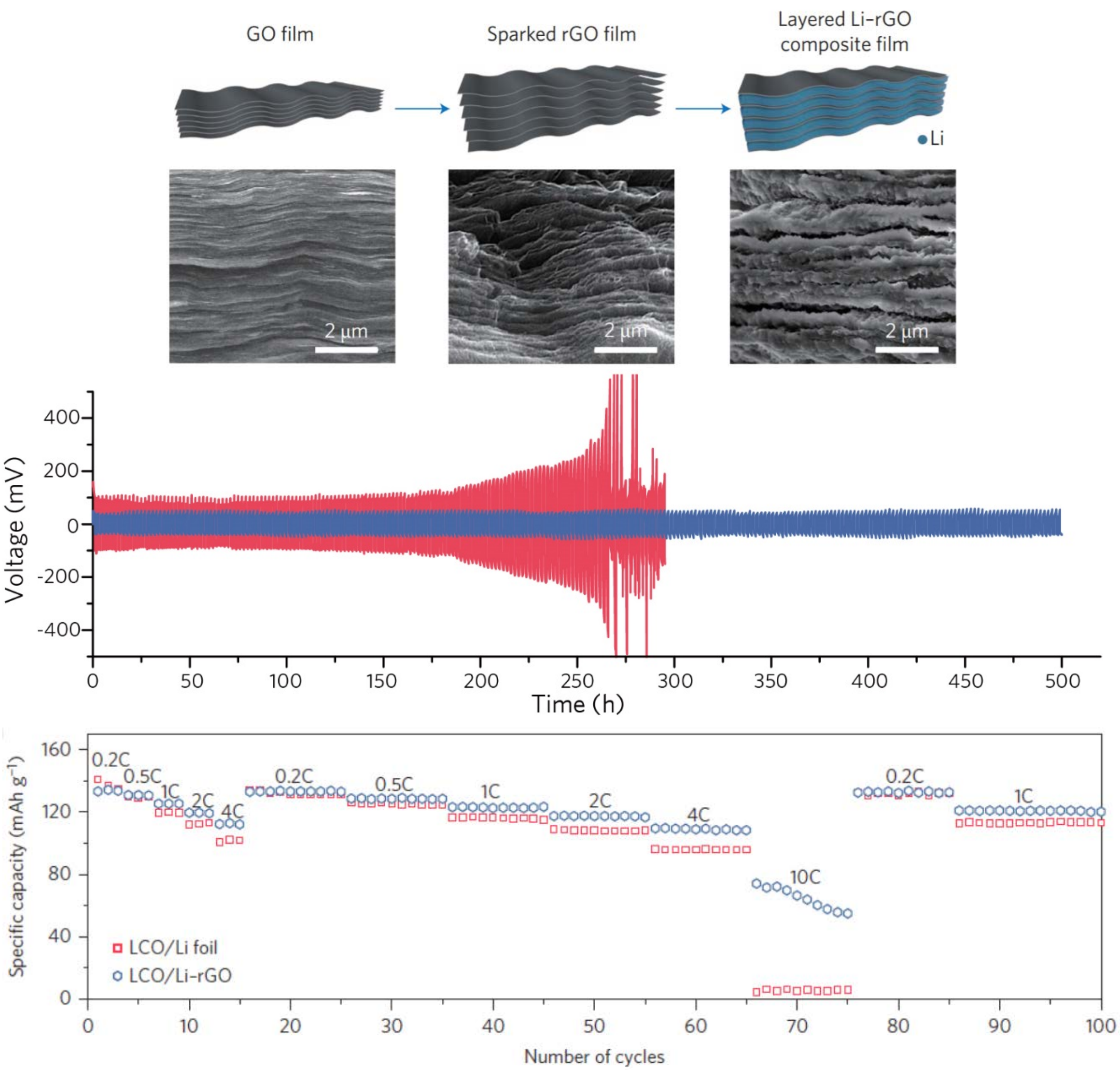
K Yan, S. Chu, Y. Cui *Nature Energy* 1, 16010 (2016)

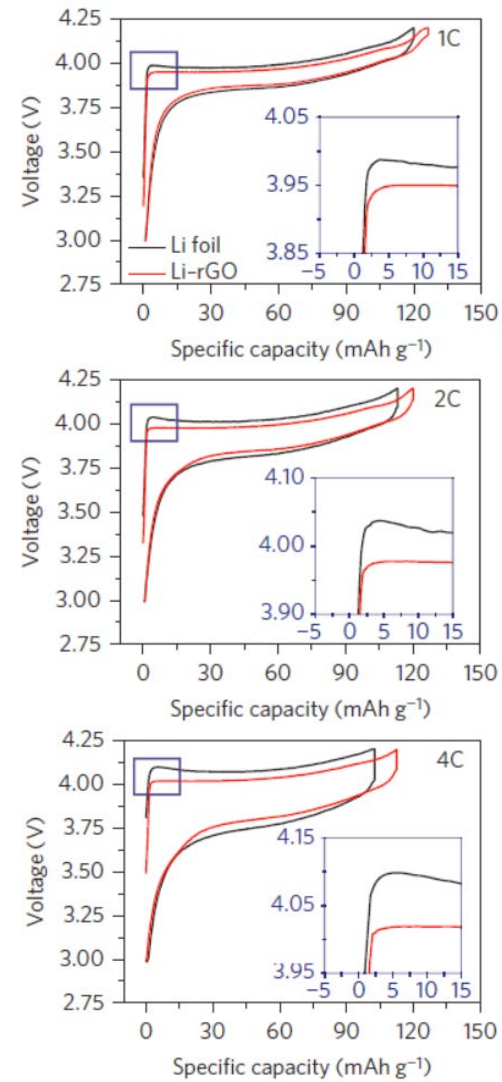

d
AuNP
200 nm
e
100 nm
f
50 nm
g
Au
C
5 nm
h
200 nm
i
200 nm
C-K
Au-M


a
Dendritic
Lithium
Carbon
Shell
10 μm
500uA/cm²
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
Voltage (V)
Capacity (mAh/cm²)
b
Lithium
Carbon
Shell w/ AuNP
10 μm
500uA/cm²
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
Voltage (V)
Capacity (mAh/cm²)

Accomplishments

Layered reduced graphene oxide as a stable host for lithium metal



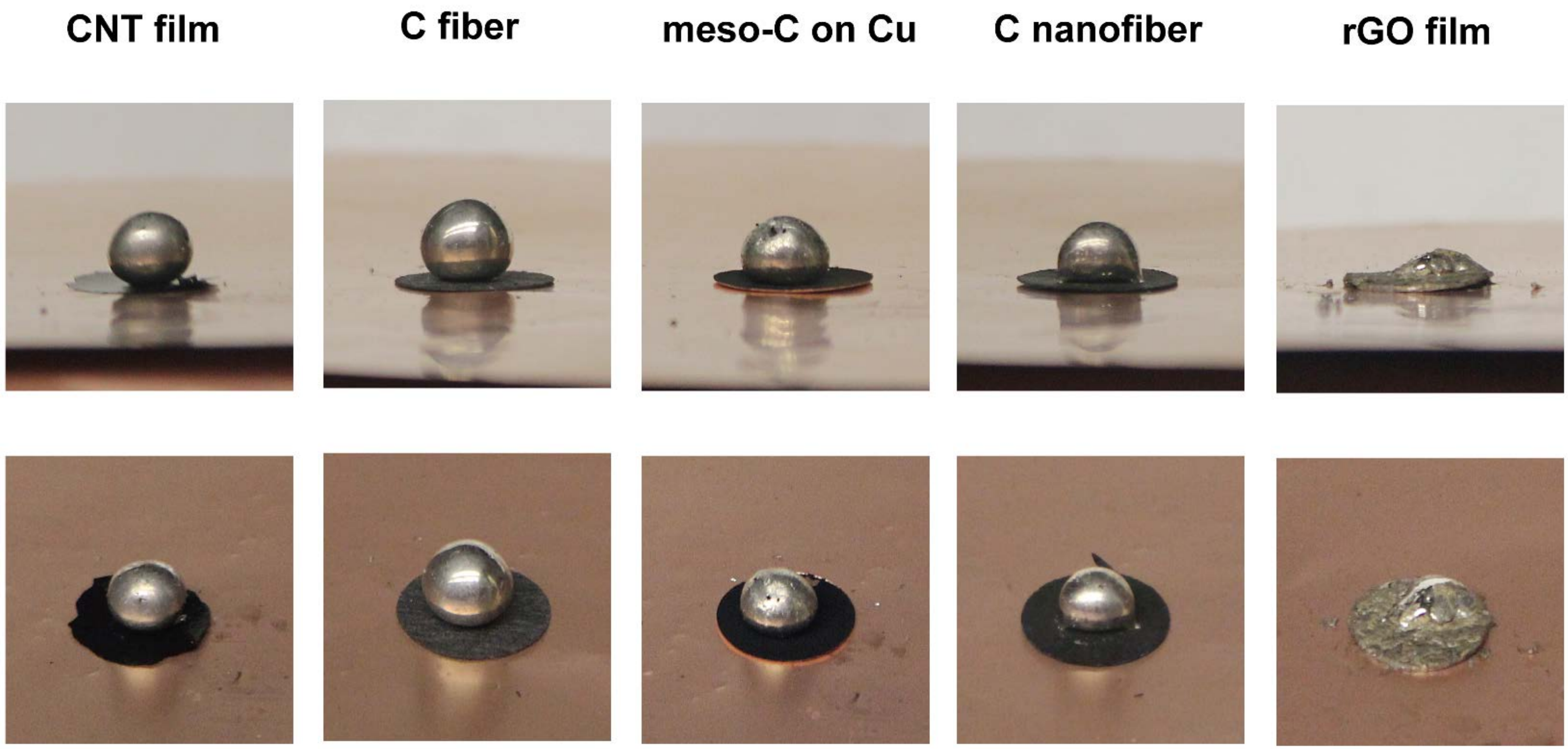


Cui group, *Nature Nanotech.* **11(7)**, 626 (2016)

Accomplishments

Layered reduced graphene oxide as a stable host for lithium metal

Make Materials Surface “Lithiophilic”

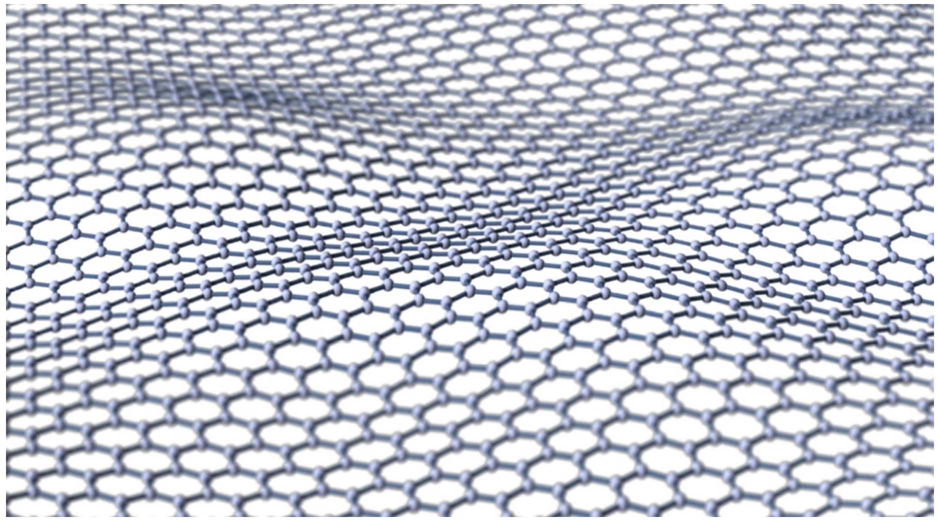


Dingchang Lin, Yayuan Liu, Yi Cui, *Nature Nanotechnology* , 11, 626 (2016)

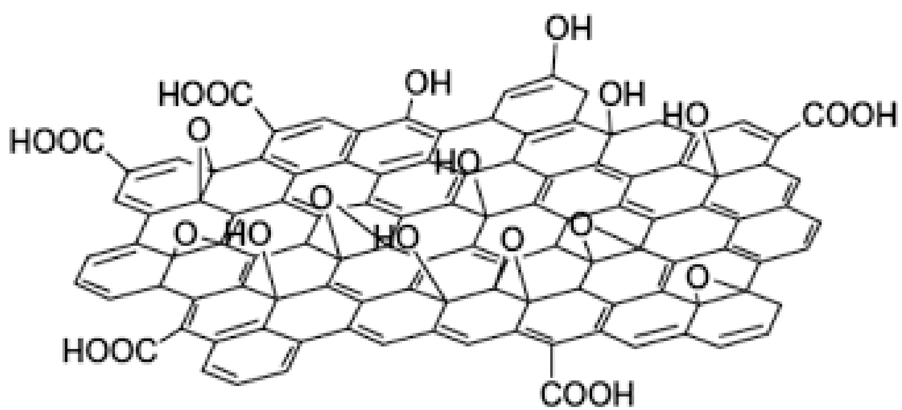
Accomplishments

Layered reduced graphene oxide as a stable host for lithium metal

Graphene



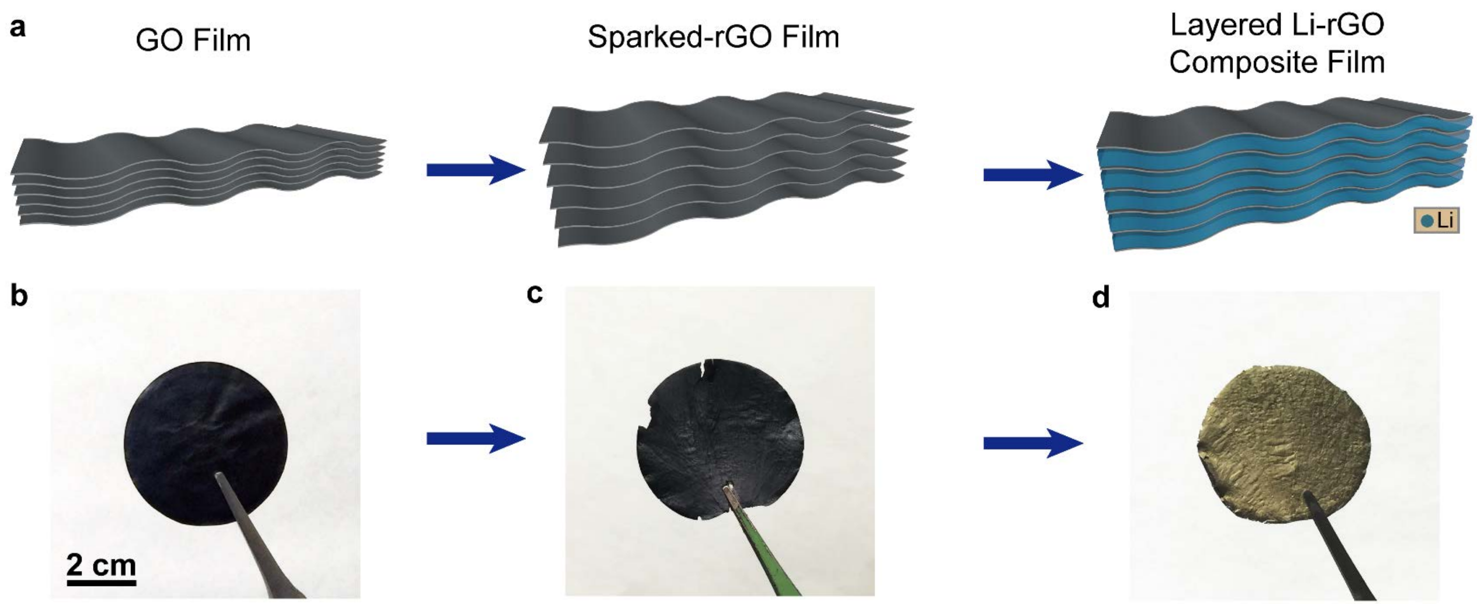
Graphene oxide



Accomplishments

Layered reduced graphene oxide as a stable host for lithium metal

Molten Lithium Infusion Into r-GO:
r-GO only 8% by weight



Dingchang Lin, Yayuan Liu, Yi Cui, *Nature Nanotechnology* , 11, 626 (2016)

Accomplishments

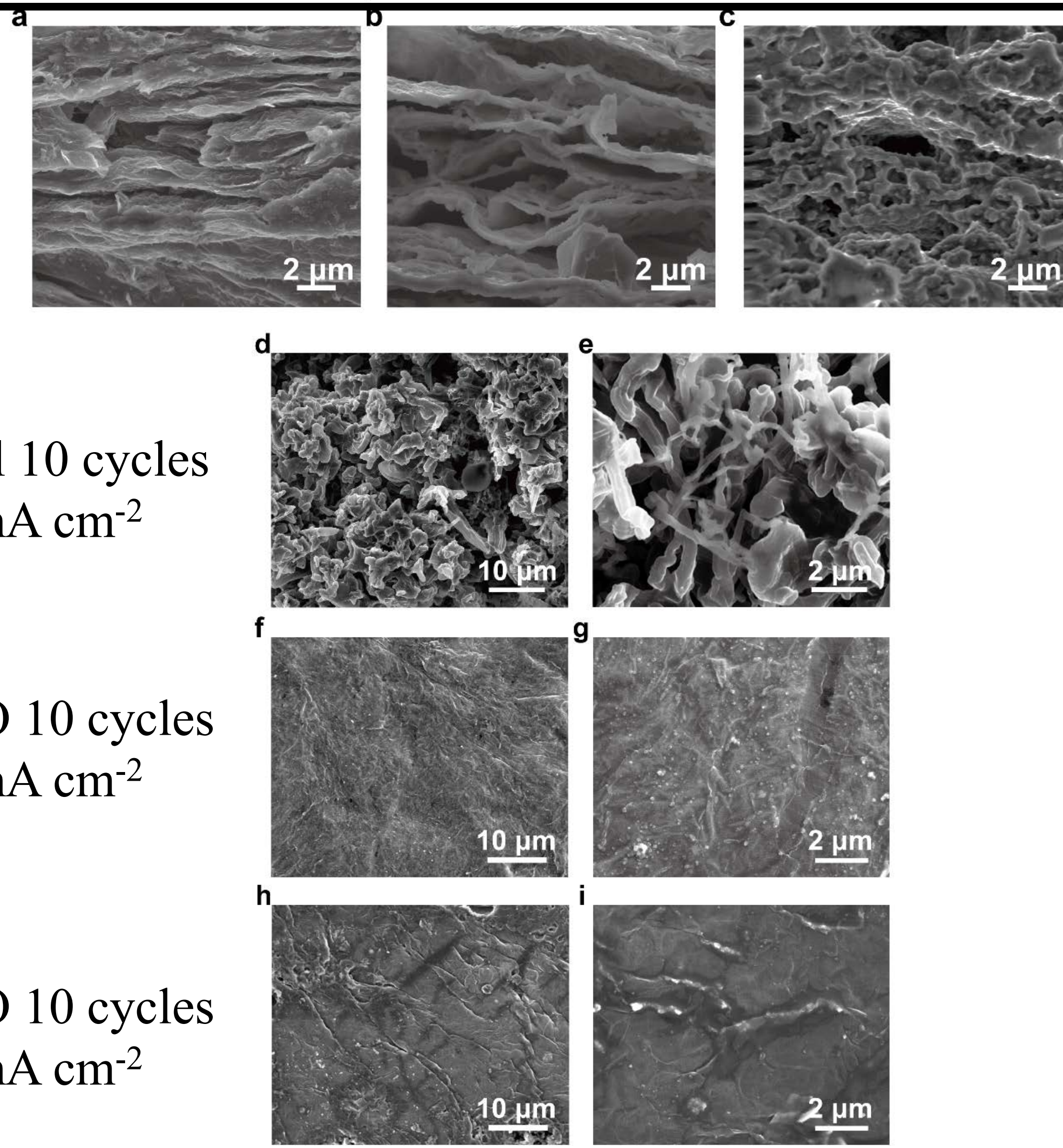
Layered reduced graphene oxide as a stable host for lithium metal

1 mA cm^{-2}

Cu foil 10 cycles
1 mA cm^{-2}

Li-rGO 10 cycles
1 mA cm^{-2}

Li-rGO 10 cycles
3 mA cm^{-2}

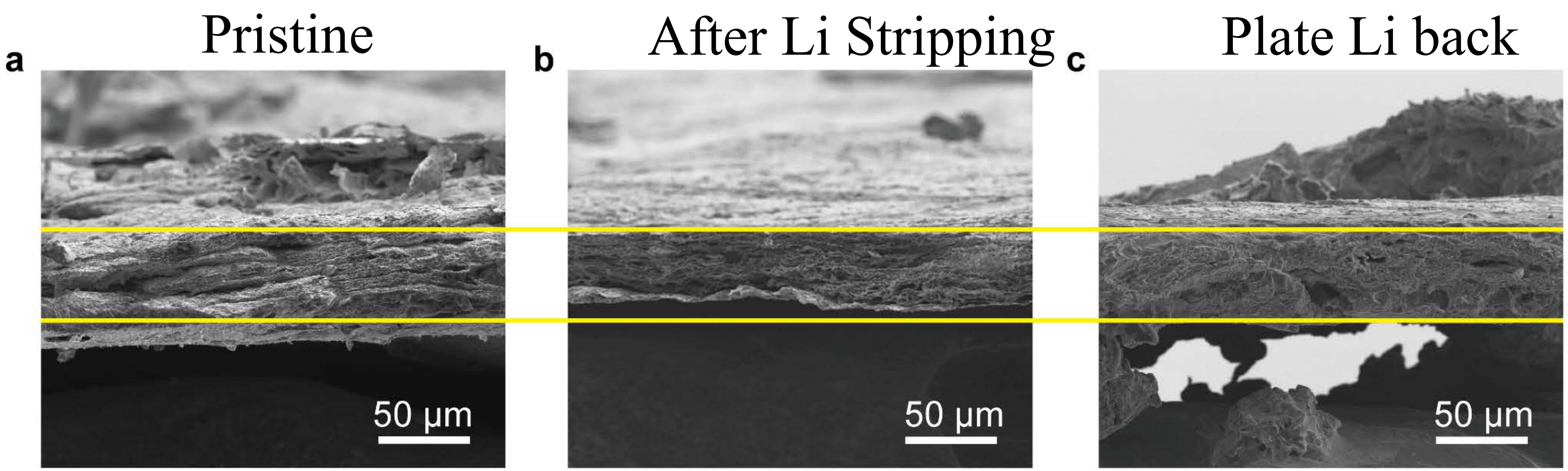


Dingchang Lin, Yayuan Liu, Yi Cui, *Nature Nanotechnology* , 11, 626 (2016)

Accomplishments

Layered reduced graphene oxide as a stable host for lithium metal

Little volume change during cycling: only 20%

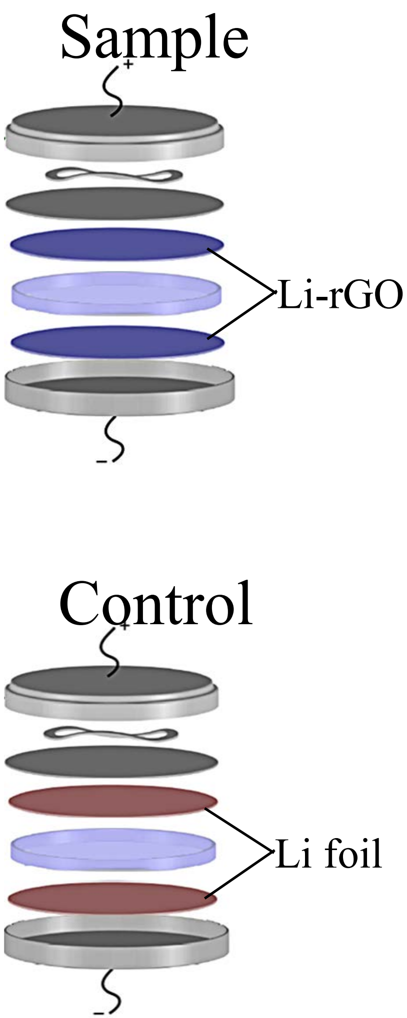


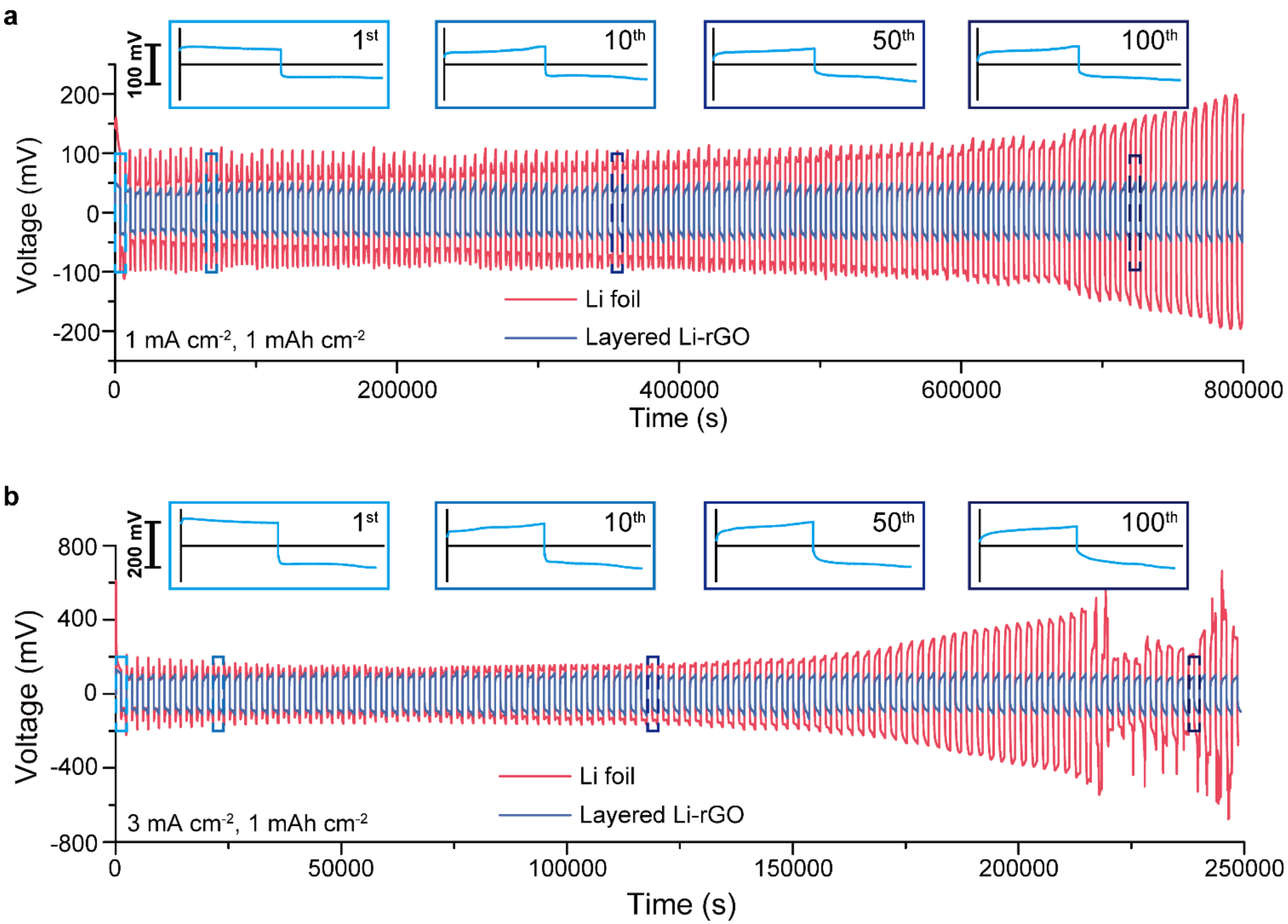
Dingchang Lin, Yayuan Liu, Yi Cui, *Nature Nanotechnology* , 11, 626 (2016)

Accomplishments

Layered reduced graphene oxide as a stable host for lithium metal

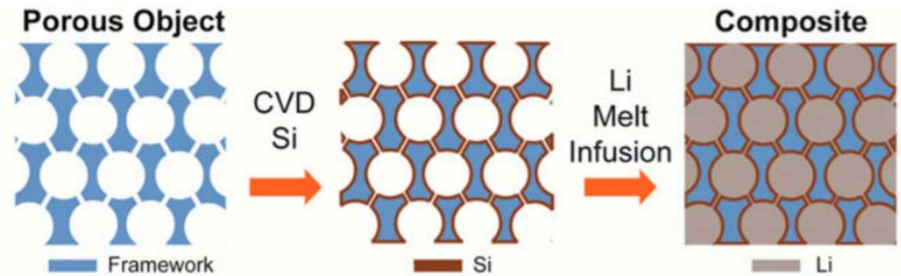
Symmetric-cell cycling in carbonate electrolyte

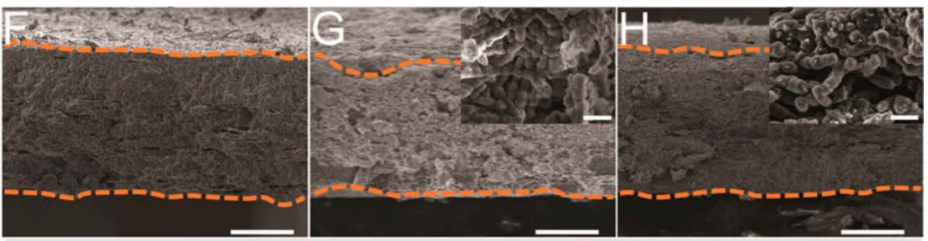


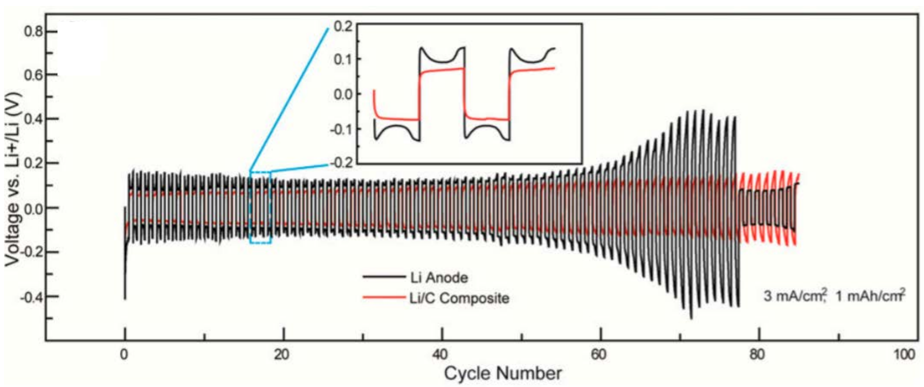


Accomplishment

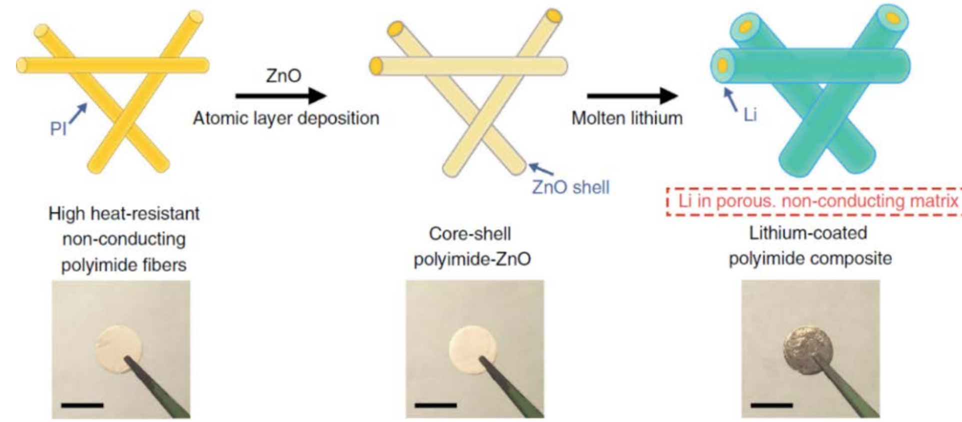
Universal silicon/ZnO coating for lithiophilic surface

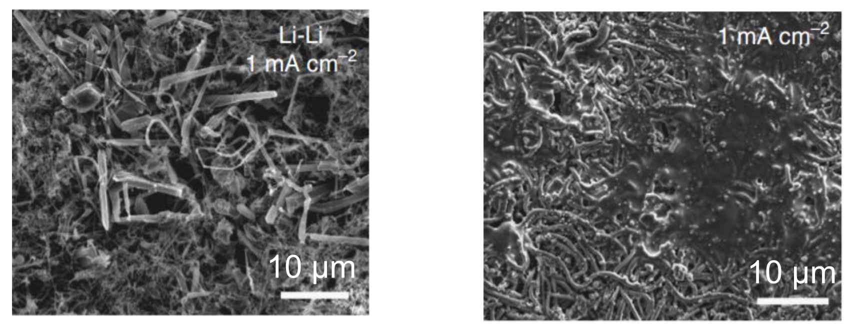


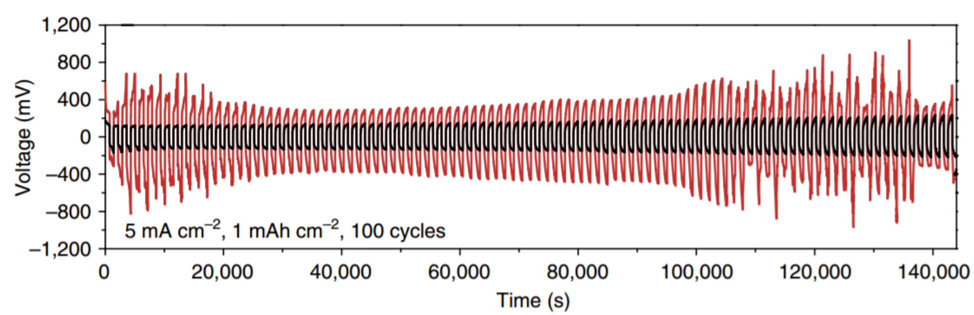




Y. Liu, Y. Cui , *PNAS*, **113(11)**, 2862 (2016)



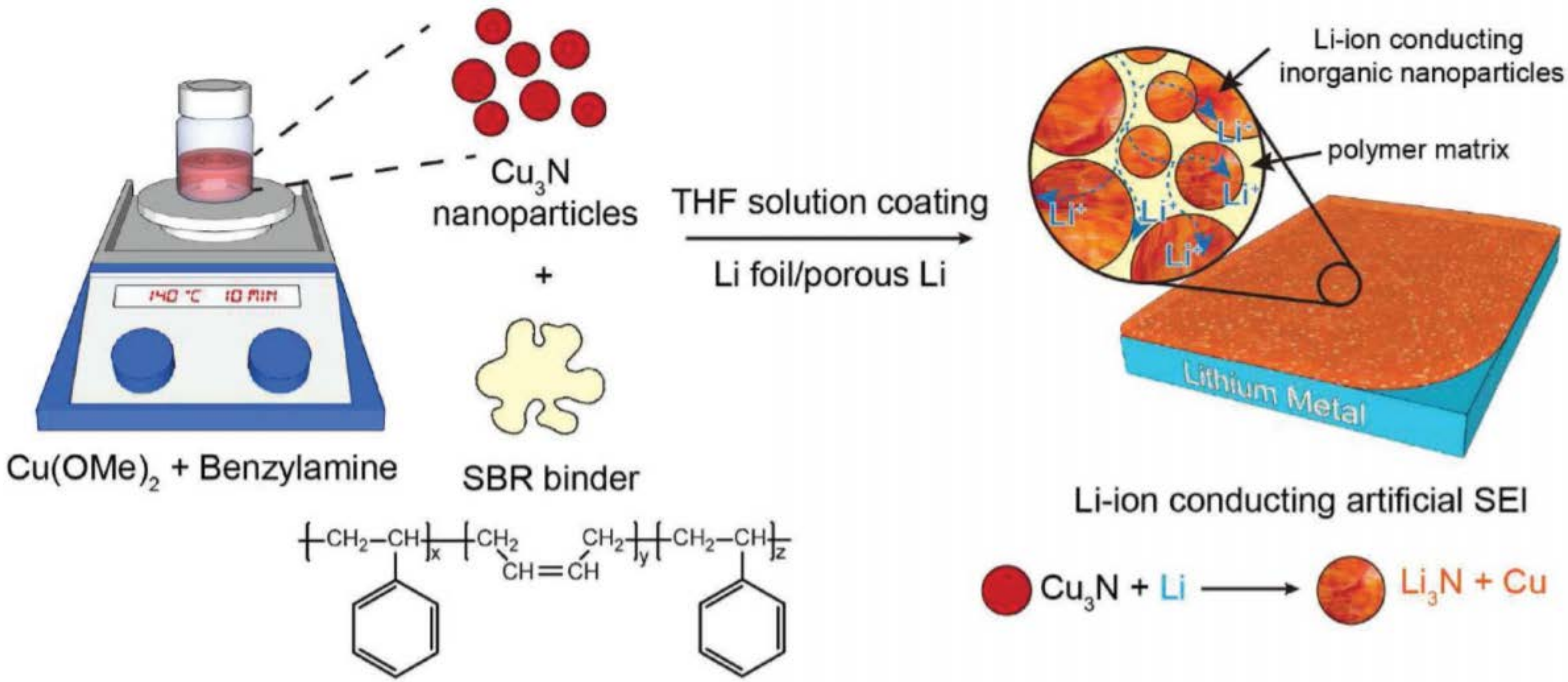


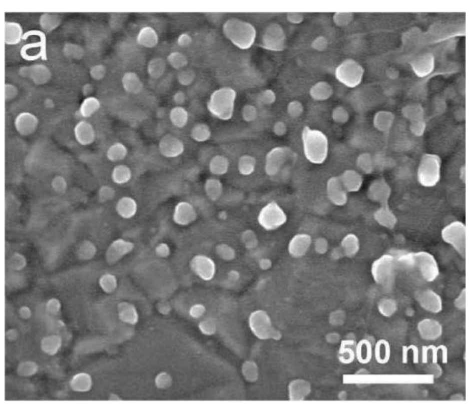


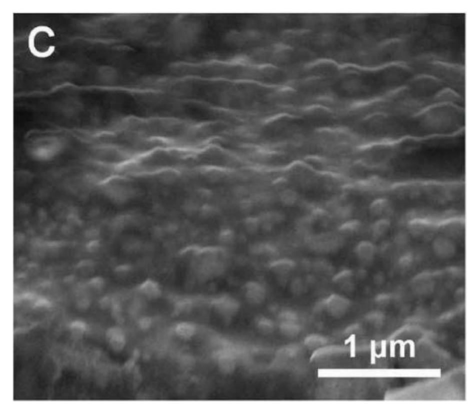
Z. Liang, Y. Cui , *Nat. Commun.* **7**, 10992 (2016)

Accomplishment

Interfacial engineering with Cu_3N-SBR composite layer-synthesis



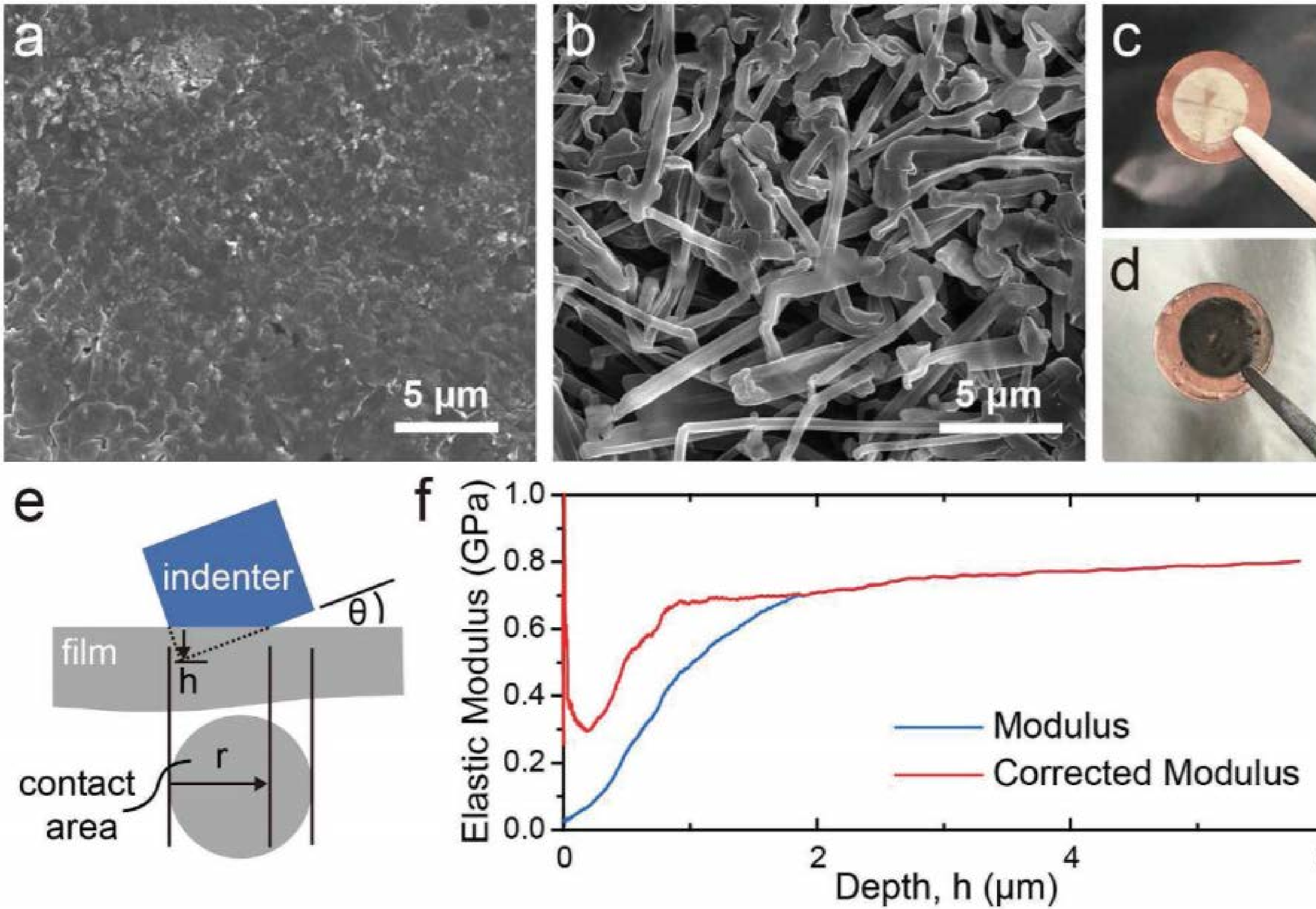




Y. Liu, Y. Cui, *Adv. Mater.*, **29,** 1605531, (2017)

Accomplishment

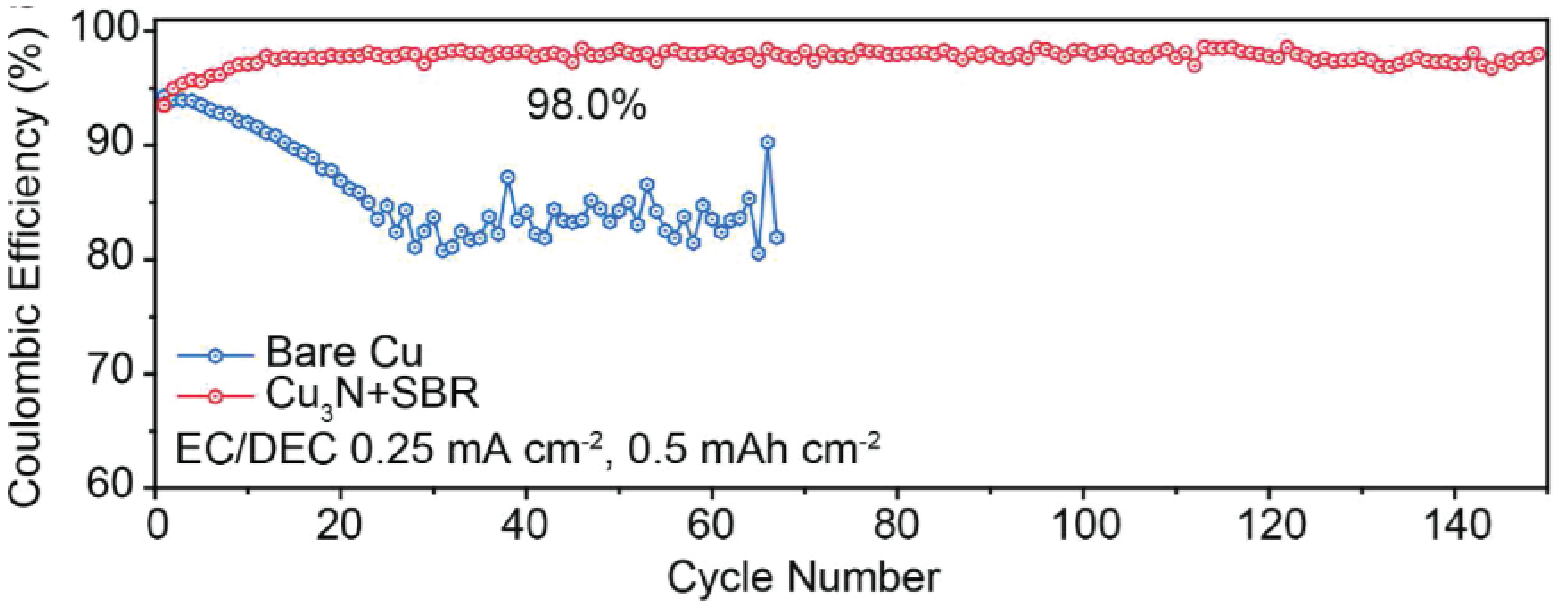
Interfacial engineering with Cu_3N-SBR composite layer -Li deposition morphology and mechanical properties



Y. Liu, Y. Cui, *Adv. Mater.*, **29,** 1605531, (2017)

Accomplishment

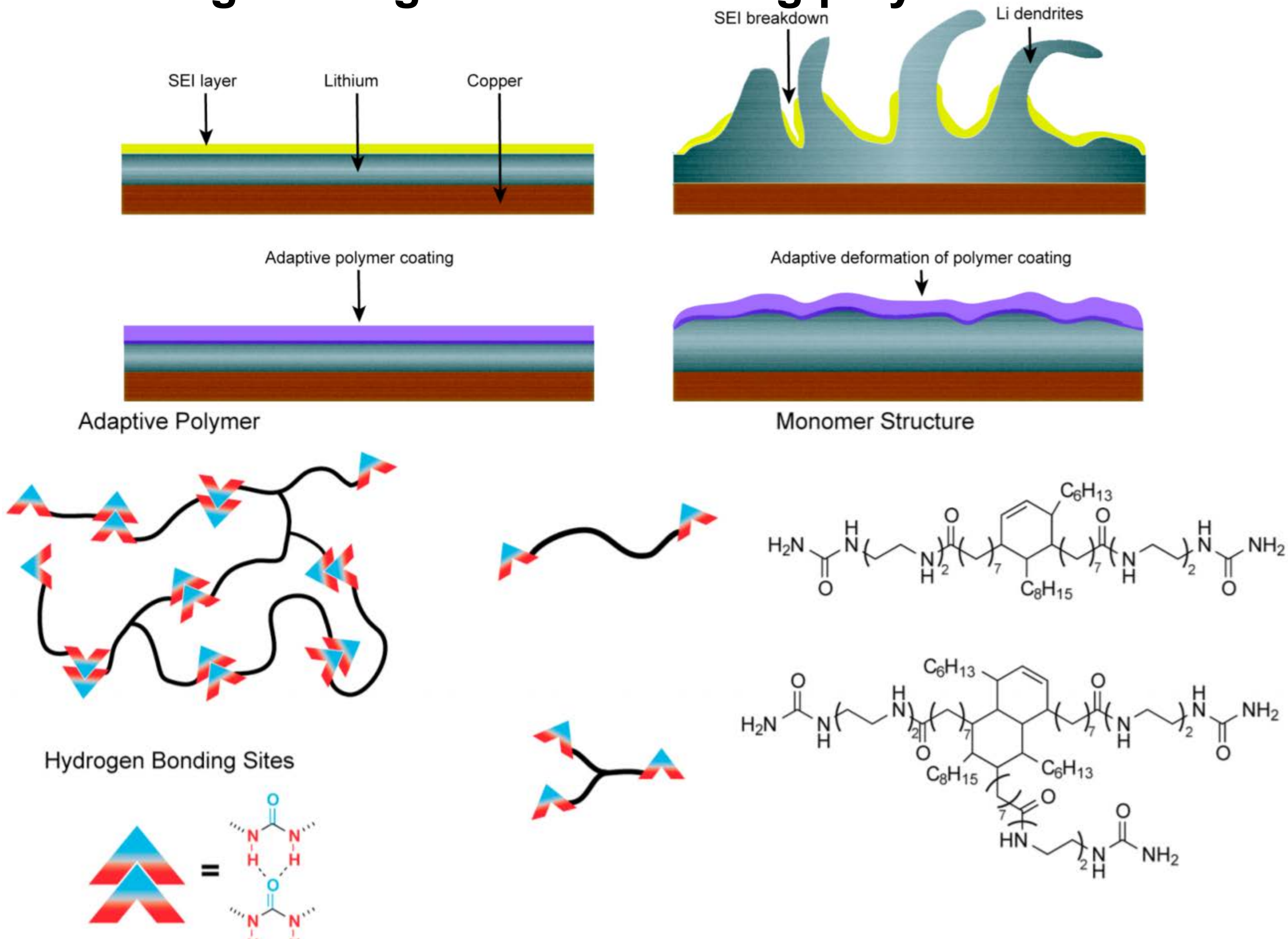
Interfacial engineering with Cu_3N-SBR composite layer
-Cycling stability



Y. Liu, Y. Cui, *Adv. Mater.*, **29,** 1605531, (2017)

Accomplishment

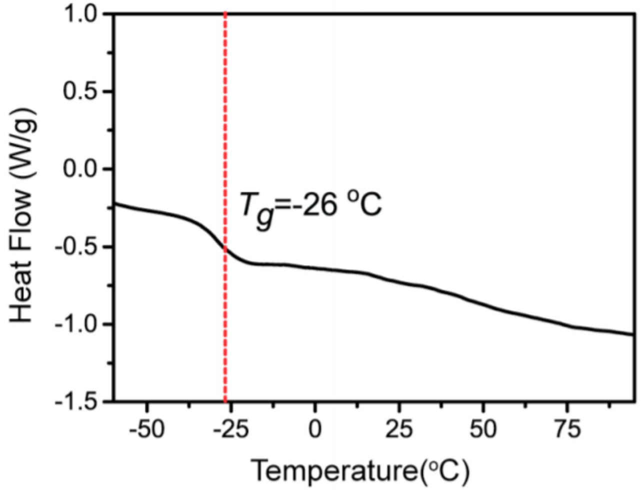
Interfacial engineering with self-healing polymer

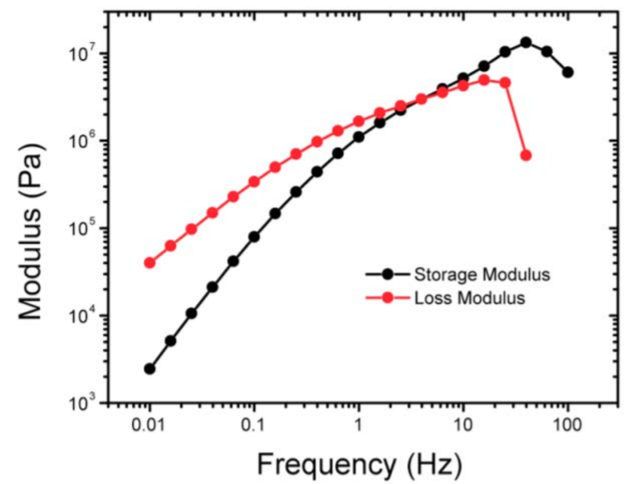


G. Zheng, Z. Bao and Y. Cui, *ACS Energy Lett.*, **1 (6),** 1247 (2016)

Accomplishment

Interfacial engineering with self-healing polymer
-Mechanical properties

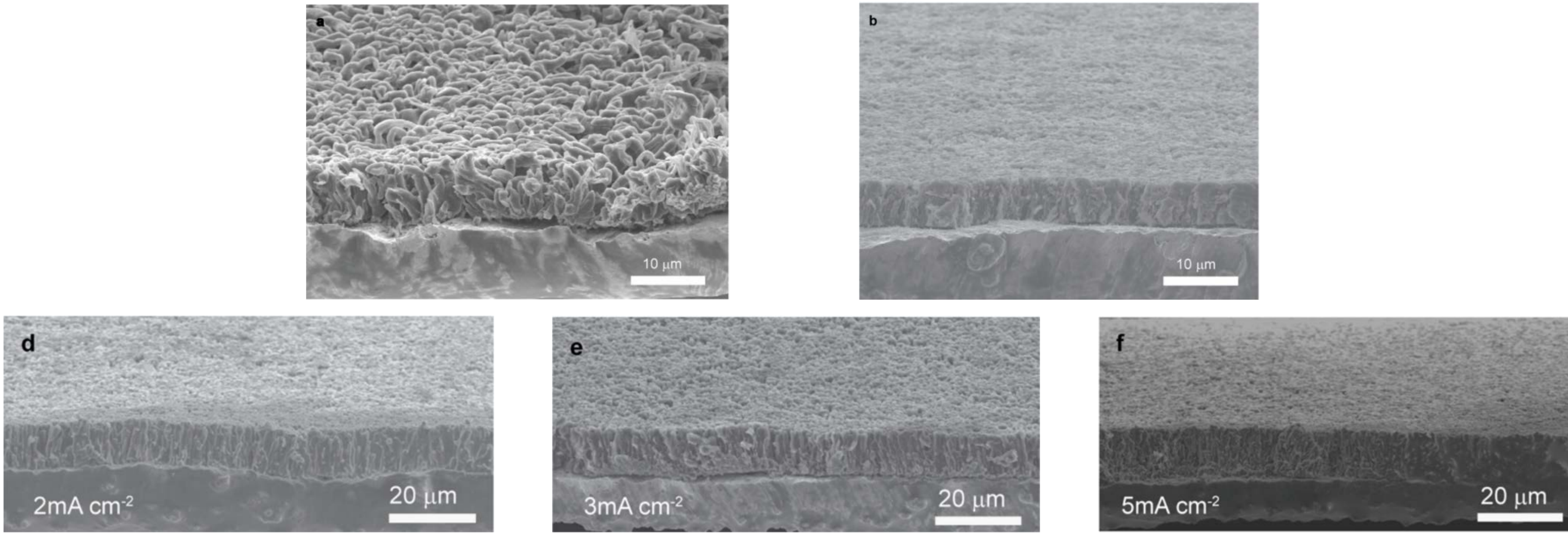


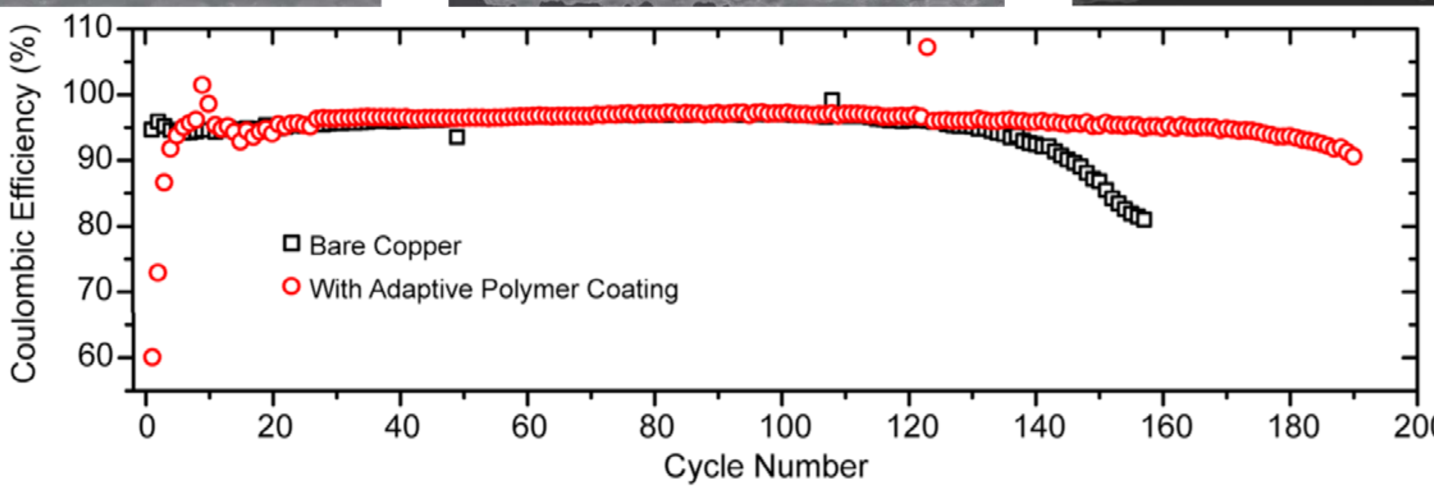


G. Zheng, Z. Bao and Y. Cui, *ACS Energy Lett.*, **1 (6),** 1247 (2016)

Accomplishment

Interfacial engineering with self-healing polymer
-Li deposition morphologies and cycling stability





G. Zheng, Z. Bao and Y. Cui, *ACS Energy Lett.*, **1 (6),** 1247 (2016)

Responses to Previous Year Reviewers' Comments

Not Applicable

Collaboration and Coordination

SLAC: In-situ X-ray, Prof. Mike Toney

Companies: Amprius Inc.

- BMR program PI’s
- Professor Steven Chu
- Professor Zhenan Bao

Remaining Challenges and Barriers

- 3D lithium metal anodes with stable interface needs to be further developed.

- Ulrahigh Coulombic efficiency needs to be achieved to minimize lithium loss during extended cycles (>99.5% for >500 cycles).

- It remains challenging to maintain even Li deposition and good cycling stability of lithium metal at ultrahigh current (>10 mA cm^{-2}).

- Integrate the stable Li metal anodes with cathode materials (NMC, sulfur, etc.) to study the compatibility and achieve high energy density

Proposed Future Work

FY 2017

-Further explore the host materials and their surface chemistry

-To integrate stable interface coating into the stable host for lithium metal.

FY 2018

-To further improve the Coulombic efficiency of lithium metal cycling and achieve practical applications (>99.5%).

-To achieve more stable cycling of lithium metal at high current density (15-20 mA cm^{-2}).

-Pair the stable lithium metal anode with cathode materials (NMC, sulfur, etc.) to make full cells.

Any proposed future work is subject to change based on funding levels.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity lithium anodes from the perspective of nanomaterials design to enable the next-generation lithium metal-based batteries to power electric vehicles, which is highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanomaterials synthesis, characterization, battery assembly and testing, which has been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key challenges in lithium metal anodes, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.